N99/420/H(3)M

INTERNATIONAL BACCALAUREATE
BACCALAURÉAT INTERNATIONAL
BACHILLERATO INTERNACIONAL

MARKSCHEME

November 1999

CHEMISTRY

Higher Level

Paper 3

19 pages

OPTION C – HUMAN BIOCHEMISTRY

C1. (a) ***[1 mark]*** each for alkanol (hydroxy) and alkene ***[2 marks]***

(accept "alkyl" as one of the functional groups)

(b) Vitamin C is water-soluble because it is very polar, ***[1 mark]***
and can hydrogen bond to water molecules, ***[1 mark]***
vitamin A is fat-soluble as it contains a long carbon chain so is much less polar. ***[1 mark]***

OR

Vitamin C is water-soluble because it has 4 OH groups ***[1 mark]*** that can hydrogen bond with water molecules ***[1 mark]***. Vitamin A is fat-soluble because it contains mostly hydrocarbon (and only 1 OH group) ***[1 mark]***.

(If the candidate states vitamin A is fat soluble and vitamin C is water soluble, but no explanation is given or the explanation is incorrect, award ***[1 mark]***)

(c) Vitamin A deficiency: night blindness ***[1 mark]***
Vitamin C deficiency: any one from: bleeding gums, feeling of tiredness, stiff limbs, ulcers, loose teeth, bruising, slow healing of wounds, ***[1 mark]***
scurvy (accept scorbutus). ***[1 mark]***

Total [8 marks]

C2. (a) Major functions: ***[1 mark]*** each for any three from: energy source, insulation, protection and cell membrane. ***[max 3 marks]***

General formula:

$$\begin{array}{l} H_2COCOR_1 \\ \quad | \\ \;HCOCOR_2 \\ \quad | \\ H_2COCOR_3 \end{array}$$

[1 mark]

(R groups need not be different)

Similarity: Both are tri-glycerides (or triesters) (or made up from propan-1,2,3-triol joined to three fatty acids). ***[1 mark]***

Differences: In fats the fatty acids are saturated / contain no C=C double bonds. In oils one or more of the acids contains one or more C=C double bonds. ***[1 mark]***

The long saturated chains in a fat molecule are able to pack more tightly with other fat molecules / are more ordered and give higher melting points due to stronger attractive (van der Waal's) forces ***[1 mark]***

than unsaturated chains which do not pack as well (due to the electrons in the π bond(s)). ***[1 mark]***

(b) 14.2 g of iodine $= \dfrac{14.2}{254} = 0.0559$ moles of iodine (accept 0.056). ***[1 mark]***

Therefore, one mole of oil reacts with four moles of iodine $\left(\dfrac{0.0559}{0.014} = 4.0\right)$. ***[1 mark]***

The oil contains four C=C double bonds. ***[1 mark]***

Total [11 marks]

C3. (a) (i) As more substrate is added the rate increases as the enzyme can work faster to form more enzyme-substrate complex. *[1 mark]*

OR

At low substrate concentration there are plenty of active sites available and up to a certain point extra substrate molecules can use more the active sites on the enzyme.

(ii) There is a limit to the number of substrate molecules an enzyme can change into product in a given time OR the enzyme is saturated. *[1 mark]*

OR

all the actives sites on the enzyme are occupied by substrate molecules.

(iii) As more heat is applied the number of molecules possessing the necessary activation energy increases to react on collision. *[1 mark]*

(iv) At these temperatures bonds in the enzyme are broken (it becomes denatured) so that it ceases to function as a catalyst. *[1 mark]*

OR

The (tertiary and quaternary) structures of enzymes are affected by such temperatures.

OR

The enzyme is denatured above this temperature.

(b) *[1 mark]* each for pH and concentration of enzyme. (Accept presence of inhibitors or certain metal ions also.) *[2 marks]*

Total [6 marks]

OPTION D – ENVIRONMENTAL CHEMISTRY

D1. This is the trapping of heat in the atmosphere / greenhouse gases act as a one-way filter *[1 mark]*

Greenhouse gases: CH_4 or water vapour or CCl_2F_2 (**must** specify a greenhouse gas to score the mark) *[1 mark]*

The incoming short wavelength (or higher energy) solar radiation penetrates the earth, but the outgoing longer wavelength (lower energy) radiation is absorbed by greenhouse gases and reradiated towards earth, causing a rise in temperature of the atmosphere. OR Solar radiation that is radiated back from the surface of the earth is of longer wavelength (infra-red radiation). *[1 mark]*

This is absorbed by the greenhouse gases in the atmosphere and prevented from escaping (so the heat is retained in the atmosphere). *[1 mark]*

Particulates reflect sunlight, thus reducing earth's temperature (or reduce the amount of radiation reaching the earth's surface). *[1 mark]*

Total [5 marks]

D2. (a) Fresh water is treated to remove suspended particles, *[1 mark]*

and remove/destroy objectionable odours (accept 'to remove soluble material'). *[1 mark]*

(Also accept removal of metal ions such as Ca^{2+}, but not heavy metal ions)

(b) Primary treatment: consists of filtering, flocculation and sedimentation (adding of chemicals such as $Al_2(SO_4)_3$ to speed up sedimentation) *[1 mark]*

Involves holding tanks or ponds where sewage is allowed to settle and solids removed as sludge *[1 mark]*

Secondary treatment consists of biological processes that use bacteria to break down organic materials (accept filters and activated-sludge process) *[1 mark]*

Tertiary treatment consists of one or more specialised chemical and/or physical processes. *Accept any two of:* carbon bed/charcoal filter, ion-exchange, chemical precipitation, reverse osmosis, electrodialysis. *[1 mark]*

Primary: Removes suspended particles OR insoluble material (such as rubbish, soil particles). *[1 mark]*

Secondary: Removes most of the organic matter. *[1 mark]*

Tertiary: Charcoal filtration removes organic molecules difficult to remove by other means OR nitrates by reverse osmosis OR… *[1 mark]*

Phosphates and nitrates need advanced treatment to be removed because these are water soluble (not removed in earlier treatment) **and** due to increasing concern about the health risks posed. *[1 mark]*

Total [10 marks]

D3. $:\ddot{\underset{..}{O}}-\ddot{O}=\underset{..}{\ddot{O}} \longleftrightarrow :\ddot{O}=\ddot{O}-\underset{..}{\ddot{O}}:$ (need both for mark) ***[1 mark]***

Oxygen's double bond is stronger than ozone's 1½ bonds.

OR oxygen has bond order of 2 whereas ozone has 1.5

OR Ozone's bonds are weaker than in oxygen's double bond because of 1.5 bonds (or 1.5 bond order) due to resonance

OR Oxygen has two electron pairs between the nuclei holding these closer together (compared to ozone) ***[1 mark]***

Thus more energy is required to dissociate it compared to O_3 ***[1 mark]***

Since $E \alpha \frac{1}{\lambda}$, then it requires light (or energy) of shorter λ ***[1 mark]***

Total [4 marks]

D4. The primary pollutants of photochemical smog are:

oxides of nitrogen (accept NO_X) and volatile organic compounds or hydrocarbons (HCs) (***[1 mark]*** for each) ***[2 marks]***

Main source: internal combustion engines ***[1 mark]***

$NO_2 \rightarrow NO + O$; $O + O_2 \rightarrow O_3$ (***[1 mark]*** for each equation) ***[2 marks]***

Sunlight decomposes NO_2 to produce oxygen free radical (photodissociation). ***[1 mark]***

(This then reacts with atmospheric oxygen to form ozone.)

Total [6 marks]

OPTION E – CHEMICAL INDUSTRIES

E1. (a) Alloys: Stainless steel OR titanium steel OR Cr steel OR… *[1 mark]*
Use: Cutlery, sinks etc., OR gas turbines, spacecraft OR ball bearings OR… *[1 mark]*

(b) Polymers: Polythene OR silicone OR PVC OR… *[1 mark]*
Use: Plastic bags, bottles etc., OR high temperature gaskets OR pipes OR… *[1 mark]*

(c) Chloro-alkali products: Sodium hydroxide OR Cl_2 (or $CaCO_3$) *[1 mark]*
Use: Soap manufacture, OR Al industries *etc.*, OR manufacture of bleach (or disinfectant), OR PVC manufacture, OR… *[1 mark]*

(accept H_2, even though it is a by-product, and its use in the Haber process)

Total [6 marks]

E2. (a) K_c decreases with temperature (or less products with increasing temperature OR increasing temperature favours reverse reaction); *[1 mark]*
thus exothermic reaction *[1 mark]*

(b) At high temperature K_c is low, thus less [Product] *[1 mark]*
at low temperature K_c is high (high [Product]) but reaction is slow *[1 mark]*
A catalyst lowers the activation energy (allowing more particles to participate in the reaction) *[1 mark]*

Total [5 marks]

E3. Catalytic cracking: converts heavier or long (high molar mass) alkanes or hydrocarbons to lighter / smaller or short-chain molecules using a catalyst. *[1 mark]*

The lighter hydrocarbons (are more easily vapourised) more useful as gasoline and in greater demand. *[1 mark]*

$C_{12}H_{26} \rightarrow C_9H_{20} + C_3H_6$
(or $C_{12}H_{26} \rightarrow C_8H_{18} + 2C_2H_4$ OR **any** acceptable cracking equation)

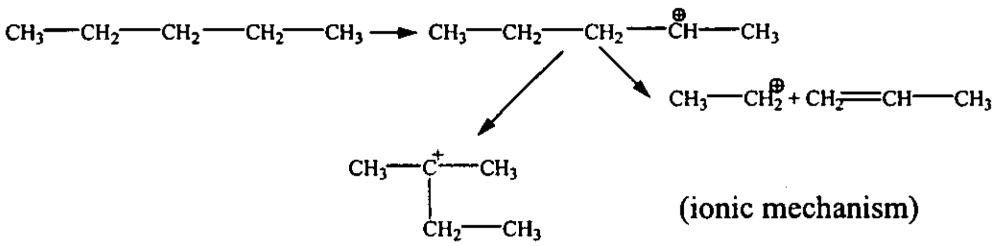
Condition: Requires heat

[1 mark] for appropriate starting material
[1 mark] for products (must be an alkane and alkene)
[1 mark] for balancing the equation
[1 mark] for condition

continued…

Question E3 continued...

Mechanism: Using zeolite as catalyst or (finely divided) silica-alumina (accept silica or alumina) *[1 mark]*



[1 mark]

[1 mark]

(ionic mechanism) *[1 mark]*

(*[1 mark]* for stating the catalyst, *[1 mark]* for formation of carbocation, *[1 mark]* for cracking to form smaller fragments, *[1 mark]* for showing rearrangement; equations need not be balanced; marks should be given if students have an idea.)

OR Accept answers in words rather than equations:
A (powdered) catalyst containing silica and/or alumina is used *[1 mark]*
The first step involves formation of a carbocation *[1 mark]*
This can undergo fission at C–C bond to give an alkene and another carbocation *[1 mark]*
which can undergo rearrangement or interact with other hydrocarbons to form an alkane (often branched) *[1 mark]*

If students show free radical mechanism which is for thermal cracking rather than ionic mechanism, give a maximum of 2 marks out of 3 for this part:

$R-CH_2-CH_2-R \longrightarrow R-CH_2-\dot{C}H_2 + \cdot R$ *[1 mark]*

$\downarrow$

$R\cdot + CH_2=CH_2 + \cdot R$ *[1 mark]*

Total [10 marks]

E4. n-type: Group 5 (15) element such as phosphorus, arsenic or antimony. *[1 mark]*

The Group 5 atom uses four of its five valence (or outer) electrons to form bonds with Si atoms. The 5th electron creates a negative charge (to produce n-type site) OR Arsenic atoms provide extra electrons (to produce n-type sites) to increase conductivity (of the silicon) *[1 mark]*

p-type: Group 3 (13) element such as boron OR aluminium OR gallium *[1 mark]*

(Bonds with 3 silicon atoms) producing an electron hole (or positive hole) because of one fewer electron (into which electrons pass, so increasing conductivity of silicon) *[1 mark]*

Total [4 marks]

OPTION F – FUELS AND ENERGY

F1. (a) Coal and oil formed from plant and marine organisms or dead organic matter *[1 mark]*

High pressure and heat (changes these into coal and oil) *[1 mark]*

OR

Remains of dead plants (coal) and sea creatures (oil) were buried, compressed and heated in the absence of air for millions of years.

(b) (i)

$$\begin{array}{rl} CO(g) \rightarrow C(s) + \tfrac{1}{2}O_2(g) & \Delta H_1 = +111\text{ kJ} \\ \underline{C(s) + 2H_2(g) + \tfrac{1}{2}O(g) \rightarrow CH_3OH(l)} & \Delta H_2 = -239\text{ kJ} \\ \underline{CO(g) + 2H_2(g) \rightarrow CH_3OH(l)} & \Delta H = \Delta H_1 + \Delta H_2 \\ & \quad = -128\text{ kJ} \end{array}$$

[1 mark] to set up equations

[1 mark]

(unit must be included to score mark)

OR $\Delta H_f = \sum \Delta H_{f(\text{product})} - \sum \Delta H_{f(\text{reactant})}$
$= -239 - (-111)$ *[1 mark]*
$= -128\text{ kJ}$ *[1 mark]*

(ii) $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$ *[1 mark]*
(must be balanced for mark; states not required)
(accept $CH_3OH + 1\tfrac{1}{2}O_2 \rightarrow CO_2 + 2H_2O$)

(iii) $Q = ms\Delta T$
$= 500\text{ kg} \times 4.18 \dfrac{\text{kJ}}{\text{kg °C}} \times (100.0 - 25.0)\text{ °C}$
$= 1.57 \times 10^5\text{ kJ}$ (accept 156750 kJ) *[1 mark]*

(iv) $\Delta H\,(CH_3OH) = -715.0\text{ kJ mol}^{-1}$
number of moles $= \dfrac{156750\text{ kJ}}{715.0\text{ kJ mol}^{-1}} = 219.2\text{ mol}$ *[1 mark]*

therefore mass of methanol
$= n \times M_{CH_3OH} = 219.2\text{ mol} \times (12.01 + 16.00 + 4(1.01))\text{ g mol}^{-1}$
$(= 219.2\text{ mol} \times 32.05\text{ g mol}^{-1})$
$= 7.026\text{ kg}$ (or 7026 g)

accept 7.03 kg *[1 mark]*

(If $M_r = 32$, then 7.02 kg) ***Total [8 marks]***

F2. (a) ${}^{234}_{91}Pa \rightarrow {}^{0}_{-1}e + {}^{234}_{92}U$ (accept ${}^{0}_{-1}\beta$ for ${}^{0}_{-1}e$) *[1 mark]*

(b) 350 s is 5 half-lives. So fraction remaining $= \left(\dfrac{1}{2}\right)^5 = \dfrac{1}{32}$ OR … *[1 mark]*

Total [2 marks]

F3. Any three from the following, *[1 mark]* each
Through spent fuel (which is highly radioactive)
through radioactive fuel OR nuclear fuel cycle
through the cooling system
through the containment building
through the control rods

[max 3 marks]

(accept accidents or meltdown (which can release radioactive materials))

Proper storage or disposal of spent fuel
(or spent fuel stored in pools of water before proper disposal)

Radioactive fuel in (airtight), reinforced containment building OR effective shielding using concrete, lead, steel

Any two for *[2 marks]*

Use of two cooling loops OR use of a secondary cooling system

Total [5 marks]

F4. (a) Some of the mass is converted into (binding) energy
OR into energy to hold the nucleus together *[1 mark]*

(b) $\left.\begin{array}{ll}\text{L.H.S.} & 235.0439 + 1.0087 = 236.0526 \\ \text{R.H.S.} & 143.8810 + 89.9470 + 2(1.0087) = 235.8454\end{array}\right\}$ *[1 mark]*

mass loss $= \Delta m = 0.2072 \text{ g mol}^{-1}$ *[1 mark]*

Therefore mass loss per gram $\text{U}-235 = \dfrac{0.2072}{235.0439}$ g (no double jeopardy) *[1 mark]*

$(= 8.815 \times 10^{-4} \text{ g})$.

$\Delta E = \Delta mc^2$ (mass must be in kg)

$= \dfrac{0.2072}{235.0439 \times 10^3} \text{ kg} \times (2.998 \times 10^8 \text{ m s}^{-1})^2$

$= 7.923 \times 10^{10}$ J (accept 7.92×10^{10} J) *[1 mark]*

(units must be included to score point)

Total [4 marks]

F5. (a) The trend is 1:1 for the lower atomic numbers (first 20 elements), increasing to 1.5:1 for higher atomic numbers (around 80) *[1 mark]*
(Accept n:p trend increases with atomic number)

As the number of protons increases in nucleus, the forces of repulsion between protons increases (drastically). *[1 mark]*
Thus a greater number of (neutral) neutrons are required (to keep particles in the nucleus together). *[1 mark]*

(b) Because the repulsive forces due to that many protons are so large that regardless of the number of neutrons, its nucleides are unstable *[1 mark]*

(c) ${}^{1}_{1}\text{p} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\text{e}$ OR ${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n}$ *[1 mark]*
(positron emission) (electron capture)

(to increase n:p ratio requires the conversion of a proton to a neutron)

Total [5 marks]

OPTION G – MODERN ANALYTICAL CHEMISTRY

G1. (a) Three *[1 mark]*

(b)

Type of Hydrogen (order irrelevant)	Chemical shift ppm	Area under peak(s) (area for one H atom = 1)	Splitting (singlet, doublet *etc.*)
(CH_3C)	**0.9**	**3**	**triplet**
(CH_2)	**2.0**	**2**	**quadruplet/quartet**
(CH_3O)	**3.8 (/4.1)**	**3**	**singlet**

[9 marks]
one for each box

(c) (i) 3.8 peak will be the smallest peak (relative area 2) rather than the 2.0 peak OR peak at $\delta = 2.0$ would be a singlet rather than a quadruplet. *[1 mark]*

(ii) Four peaks rather than three,
OR appearance of peak at ~ 9.7 ppm *[1 mark]*
OR peaks = triplet, quartet and quartet, triplet

(iii) Four peaks rather than three,
OR appearance of peak at ~ 11.5 ppm *[1 mark]*

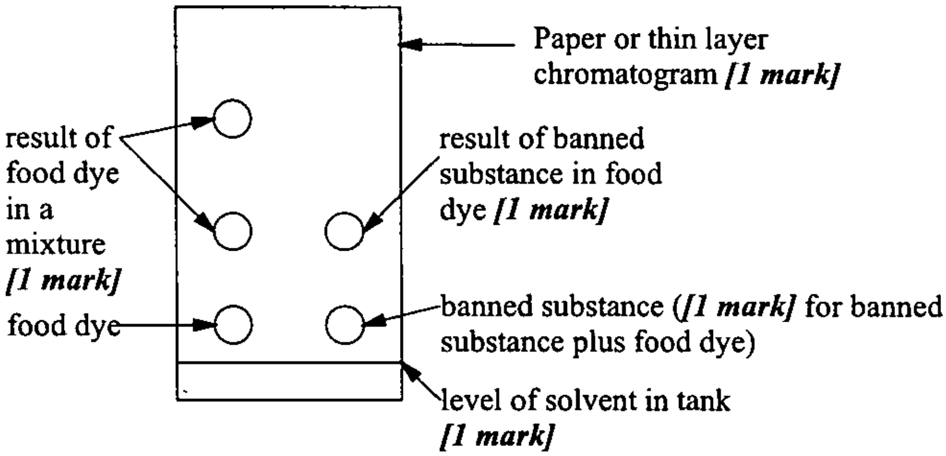
(iv) Peak at 2500 to 3300 cm^{-1} *[1 mark]*
for butanoic acid due to presence of hydrogen-bonded –OH in acids *[1 mark]*

Total [15 marks]

G2. (a) Six points, ***[1 mark]*** each:

- Paper or thin layer chromatography (also accept hplc) ***[1 mark]***
- Extract colouring matter (boil with solvent) ***[1 mark]***
- Put separately a spot of this **and the pure banned substance** on the plate ***[1 mark]***
- Elute the plate using a suitable solvent ***[1 mark]***
- If sample forms 2 or more spots it is a mixture ***[1 mark]***
- If one of the spots has travelled same distance as the banned substance then it is probably a component of the mixture ***[1 mark]***

OR



and ***[1 mark]*** for indicating extraction of colouring matter

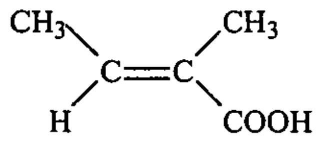
(b) Four points, ***[1 mark]*** each:

- Gas/vapour phase chromatography (glc/vpc) or high pressure/performance liquid chromatography (hplc) (accept gas-liquid chromatography) ***[1 mark]***
- Inject a (small) sample of ethanol and measure retention time ***[1 mark]***
- Inject the organic liquid into gas/liquid column and produce chromatogram. Ethanol is (probably) present if there is a peak in the liquid chromatogram at the same time as ethanol ***[1 mark]***
- The height or area of the peak compared to those of the other components of the organic liquid could indicate the relative amount of ethanol present ***[1 mark]***

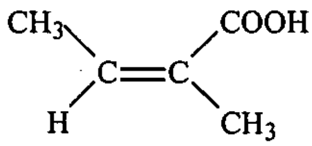
OR Use standard concentrations of ethanol and compare to area of ethanol peak in sample
(Accept glc followed by mass spec for last point) ***Total [10 marks]***

OPTION H – FURTHER ORGANIC CHEMISTRY

H1. (a)



cis-A

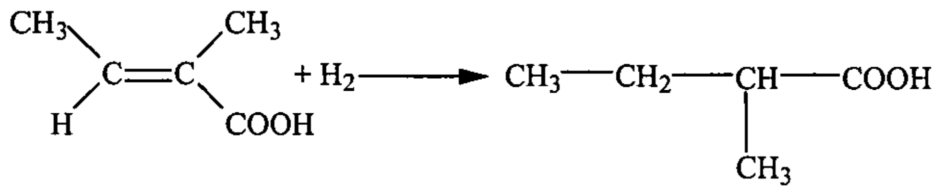


trans-A

[1 mark] each

(names not required)

(b)



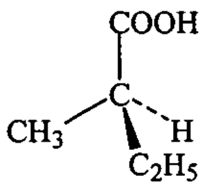
[1 mark]

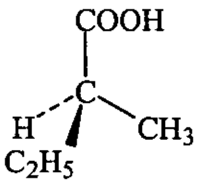
(can start with cis-A or trans-A)
Accept a balanced equation showing the correct molecular formula

(c) 2-methylbutanoic acid *[1 mark]*

(d) An optically inactive mixture of equal amounts of enantiomers *[1 mark]*

(e) Accept





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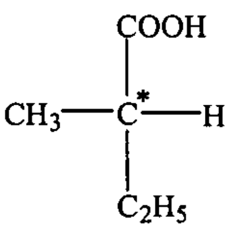
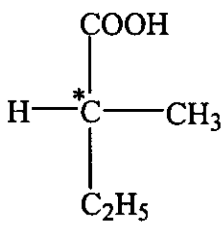




[1 mark] each

(must show mirror images; no need for * on C)

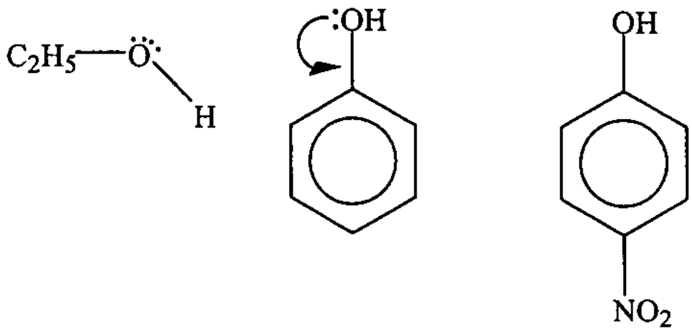
(f) These have identical physical properties except *[1 mark]*
for the direction of rotation of plane polarised light which is opposite OR differ in optical activity. *[1 mark]*

Total [9 marks]

H2. (a) Increasing acid strength:

ethanol < phenol < 4-nitrophenol *[1 mark]*

(pK_a ≈16 10.00 7.15)



(Acidity depends on the process $-O-H \rightarrow -O^- + H^+$)

Lone e^- pair on oxygen participates in ring delocalisation in phenol *[1 mark]*
e^- density on oxygen reduced (compared to in ethanol),
(thus H^+ can leave more easily), and stronger acid than ethanol *[1 mark]*

In nitrophenol, NO_2 is an electron attracting (or withdrawing) group,
(further reducing e^- density on O), and still stronger acid *[1 mark]*

(b) $H_2O > C_2H_5 \longrightarrow O-H$

(pK_a 14 ≈16)

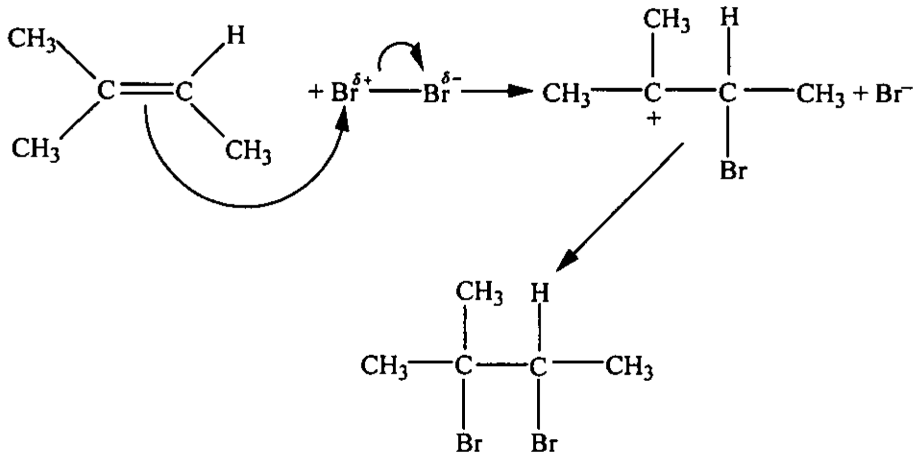
OR Water is a stronger acid than ethanol

C_2H_5 (OR *R*) group is e^- releasing (OR has an electron releasing inductive effect) *[1 mark]*

Thus electron density is greater on O in C_2H_5OH and H^+ cannot leave as easily, thus weakens acid (compared to water). *[1 mark]*

Total [6 marks]

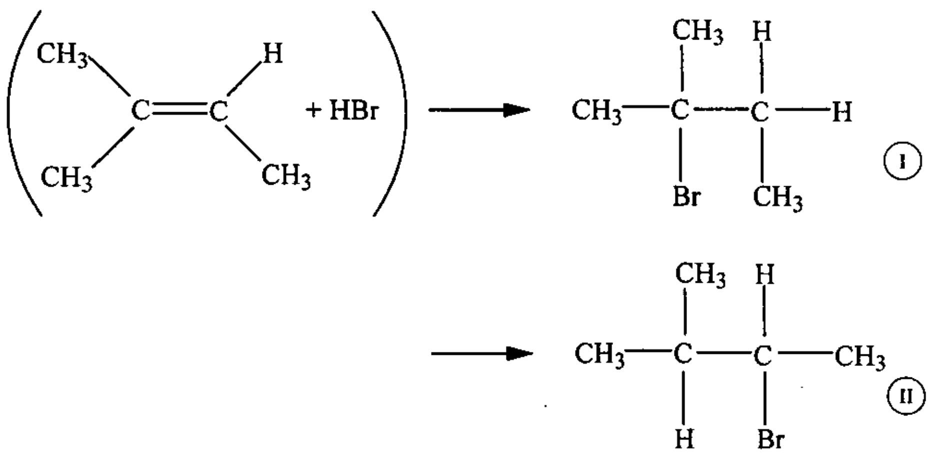
H3. (a) Electrophilic (ionic) addition *[1 mark]*



OR Step 1: Br—Br → $Br^{\delta+}$—$Br^{\delta-}$ *etc.*

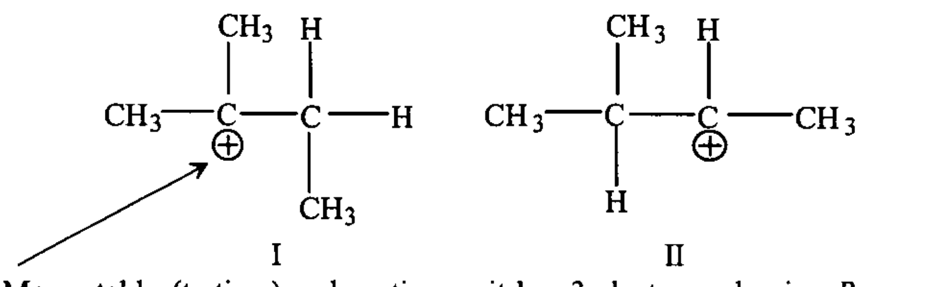
[1 mark] for induced $Br^{\delta+}$—$Br^{\delta-}$
[1 mark] for carbocation (carbonium ion) intermediate
[1 mark] for addition product

(b)



[1 mark] for each product

(c) I is the major product *[1 mark]*



[1 mark] each

More stable (tertiary) carbocation as it has 3 electron releasing *R* groups stabilising the ion (compared to only 2*R* groups on the other carbocation). *[1 mark]*
(No mark for just saying/stating Markovnikov's rule.)

Total *[10 marks]*